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Publication date:
2013

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Citation (APA):

Mekonnen, Y. S., Knudsen, K. B., Mýrdal, J. S. G., Younesi, R., Højberg, J., Hjelm, J., Norby, P., & Vegge, T. (2013). *The Influence of CO₂ Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries*. Poster session presented at Nordisk Batterikonferens 2013 (NORDBATT), Uppsala, Sweden.

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The Influence of CO₂ Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries

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Introduction

The Li-O₂ couple is particularly attractive due to its high specific energy, ~5-10 times greater than currently available Li-ion batteries and mainly intended for onboard storage in vehicles.¹ As first reported by Abraham et al. in 1996, the Li-O₂ cell with aprotic solvent is shown to be rechargeable, when Li₂O₂ is formed during discharge.² However, Li₂CO₃ is also formed from the parasitic reactions between the Li₂O₂ and aprotic electrolytes, air impurities (e.g. CO₂) and the graphite.¹ Both Li₂O₂ and Li₂CO₃ are insulating materials with wide band gap of 4.9 and 8.8 eV, respectively. Hence, these materials deposit (5-10 nm) limit the conductivity and lead to sudden death.³

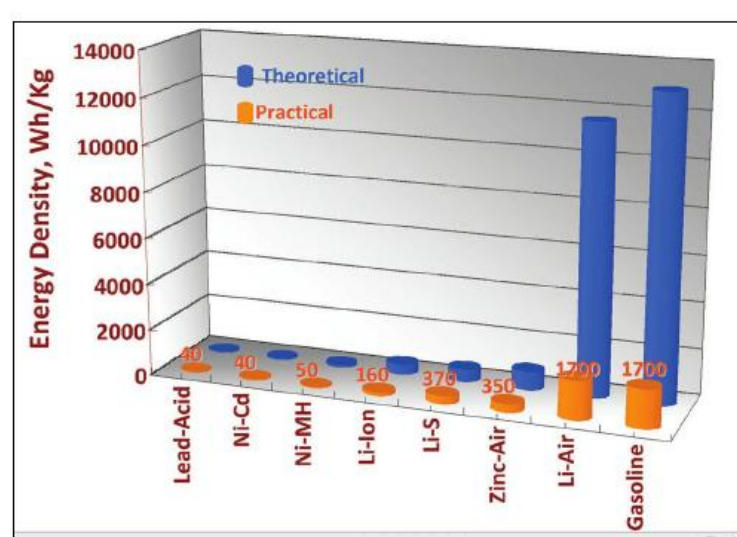


Fig1. Energy densities of M-air wrt Gasoline.

Methods

- ✓ Li-air cells were constructed using a Swagelok design. Each cell contained LiTFSI, DME and P50 cathodes. Experiments were performed using a galvanostat.
- ✓ DFT as implemented in GPAW code⁴ via ASE. RPBE approximation is used. The stepped (11̄00) Li₂O₂ surface with a super cell consisting of a 56-60 atoms slab with 18 Å vacuum layer and (4,4,1) kpoints are used.



Results

- ✓ CO₂ binds preferentially at step sites on the (11̄00) Li₂O₂ surface and blocks the active nucleation sites.
- ✓ Both DFT and experimental results show that, CO₂ contamination strongly affects the recharging process.
- ✓ Higher overvoltages and large capacity losses are observed at 50 % CO₂.

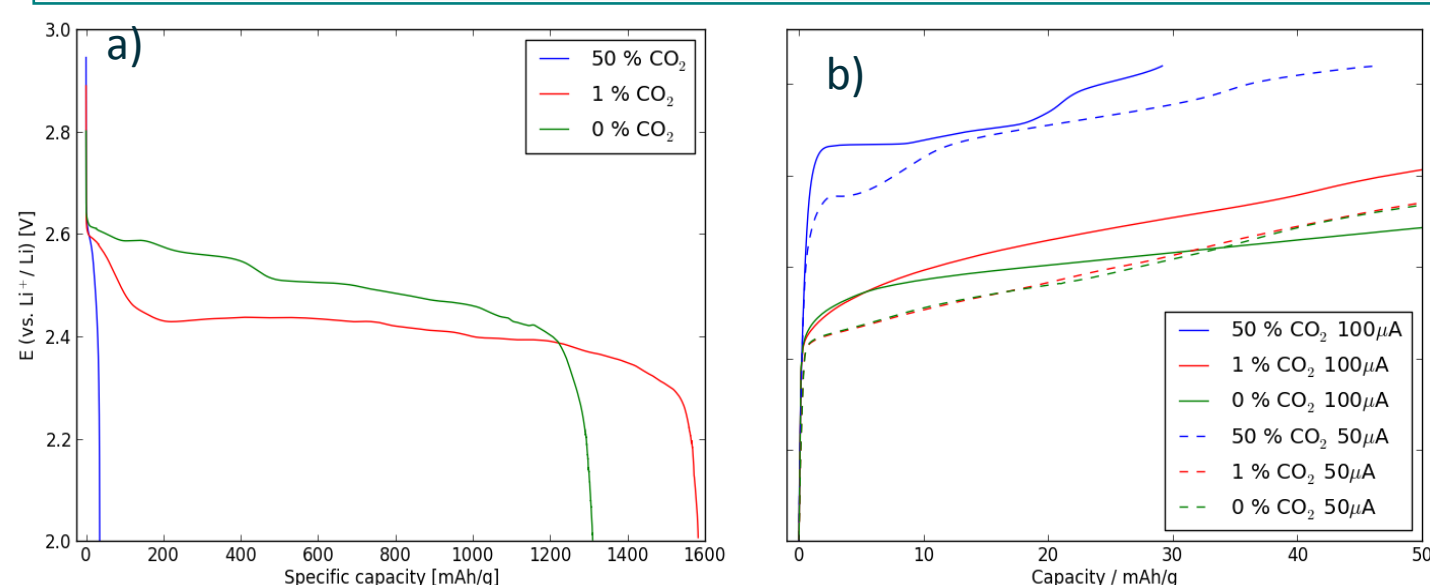
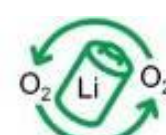


Fig2: a) Discharge, b) Charge curves for pure & CO₂ contaminated cells.

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Funded by ReLiAble Project



A four step, 2Li₂O₂, growth mechanism on (11̄00) Li₂O₂ surface⁵ with CO₂

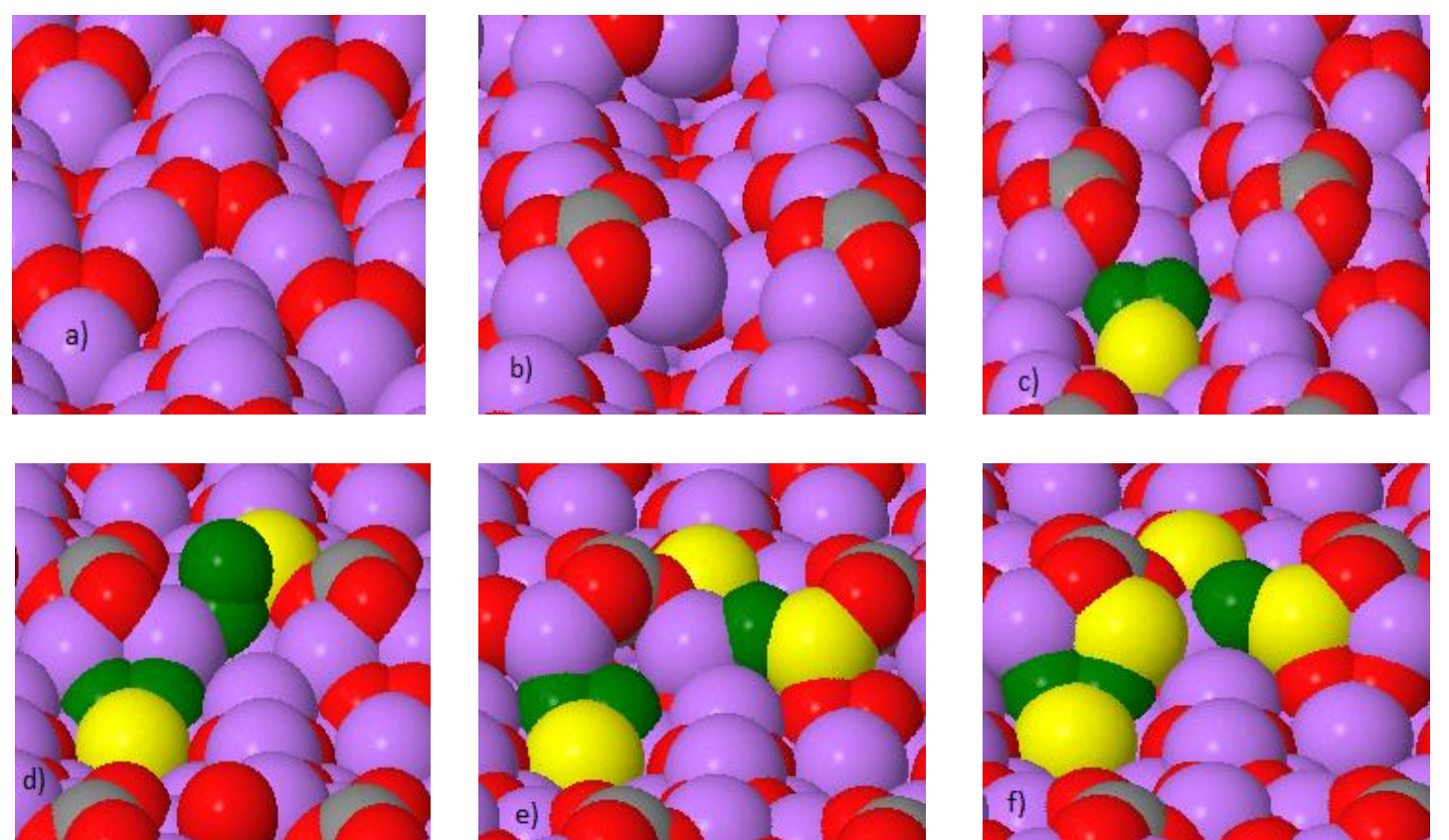


Fig3: a) Stepped Li₂O₂ surface. b) CO₂ adsorbs at step. c) 1st LiO₂ binds. d) 2nd LiO₂ binds. e) 1st Li binds. f) 2nd Li binds to the surface; end up with 2 Li₂O₂ growth.

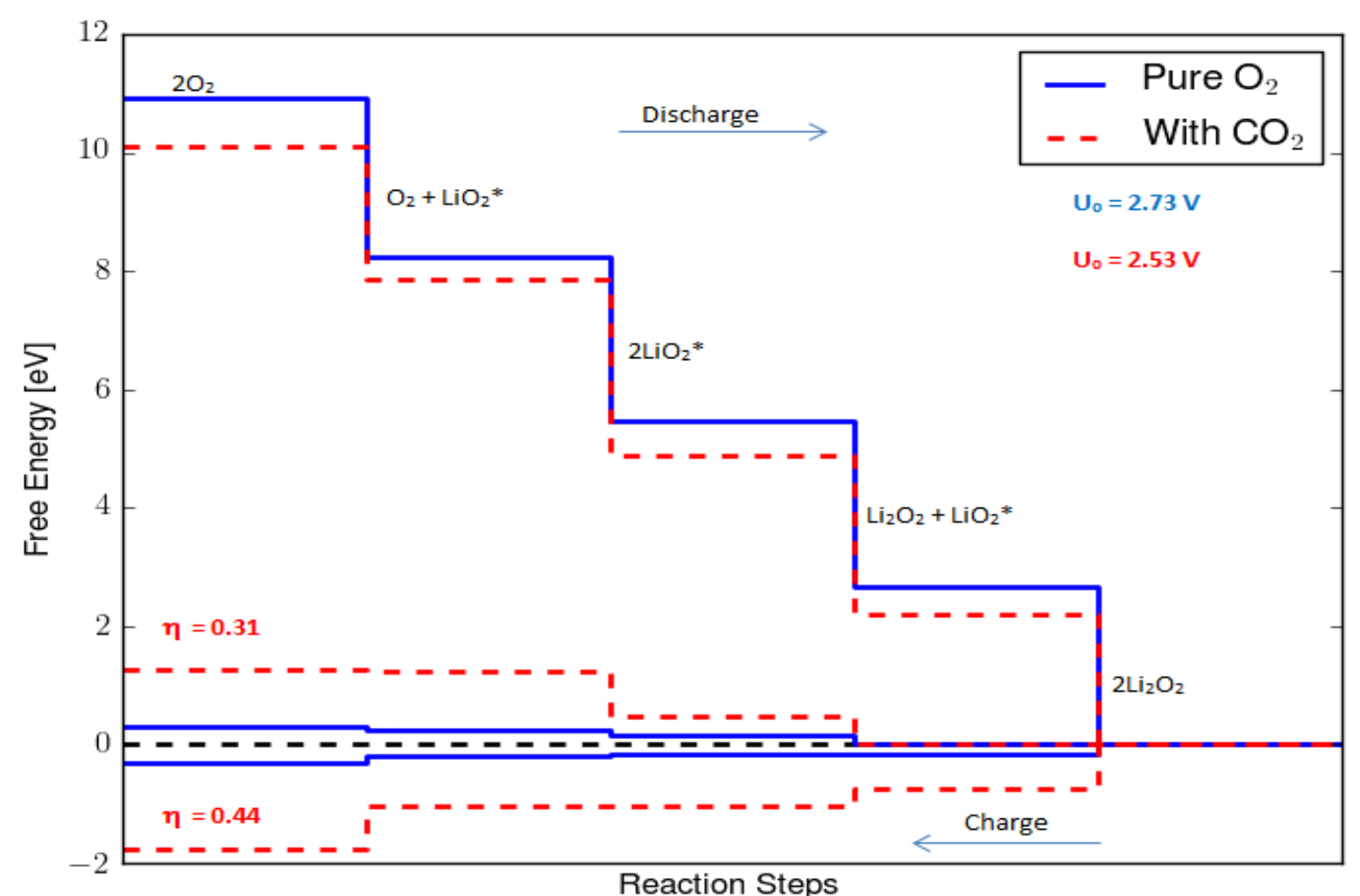


Fig4: Free energy diagrams for discharge mechanism of Li₂O₂ on Cathode surface with and without CO₂.

Conclusions

- ✓ CO₂ is the most critical due to its high solubility in aprotic electrolytes & high reactivity with Li₂O₂ to form Li₂CO₃.
- ✓ CO₂ binds favorably at steps sites on Li₂O₂ surface and once it is adsorbed at the step site, it is unlikely to diffuse elsewhere.
- ✓ The recharging process is strongly influenced by CO₂, and exhibits higher charging overvoltage, which is observed already at 1 % CO₂ while at 50 % CO₂ a large capacity loss is seen.